The potential for volatile phosphorus-containing flame retardants in textile back-coatings

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ABSTRACT

A number of volatile phosphorus-containing flame retardant species have been identified as possible replacements for bromine-containing formulations used in textile back-coatings because of the need for vapour-phase activity. The selected retardants include tributyl phosphate (TBP), a monomeric cyclic phosphonate Antiblaze CU (Rhodia Specialites) and the oligomeric phosphate-phosphonate Fyrol 51 (Akzo). When combined with an intumescent char-forming pentaerythritol derivative (NH1197, Chemtura) and applied as a back-coating on to cotton and polypropylene substrates, significant improvements in overall flame retardancy are observed. One sample applied to cotton and comprising both TBP and intumescent passed the simulated match-ignition test, BS5852:1979:Part1 after a water soak at 40^{o}C for 30 min. Determination of residual phosphorus within chars shows that there is significant volatile activity present in these formulations.

Addition of volatile nitrogen as melamine also demonstrated improved flame retardancy in similar formulations.

Keywords: Flame retardant, back-coating, textile, phosphorus, intumescent, melamine

INTRODUCTION

Since the early 1990s there has been increasing pressure on all users of flame retarded materials to reduce concentrations of, if not remove, halogen-containing flame retardants. This challenge is particularly great in textiles because of the need to address both aesthetic and durability issues while retaining high levels of flame retardancy required for fibre-containing materials where surface area-to-mass ratios are considerable. Not only does this often mean that flame retardant species have to be concentrated at fibre surfaces but also that these latter are exposed to very reactive external agencies. In the particular case of textiles for domestic furnishing fabrics, which since 1988 in the UK have been required to possess resistance to cigarette and simulated ignition sources [1], halogen-containing back-coated flame retardant finishes are considered to take about 80% of this market.

While the recent US National Academy of Science risk assessment [2] concluded that decabromodiphenyl ether or decaBDE (also known as bis(pentabromophenyl ether)) did not pose a toxicological risk and that subsequently it has passed rigorous EU toxicological risk assessment in May 2004 [3], there are still pressures to ban it based on claimed bio-accumulative properties and degradation to toxicological congeners.

In developing a phosphorus flame retardant strategy for the replacement of decaBDE and similar bromine-based formulations, it is evident that the vapour-phase activities of these latter are key factors in determining their efficiency apart from their excellent insolubility and general intractability. Notwithstanding these prime issues, the outcomes of our previous research [4, 5] have led to three strategies that may be used in achieving these requirements:

1. the sensitisation of decomposition or flame retarding efficiency of phosphorus-based systems;
2. the reduction in solubility of successful but soluble systems and

3. the introduction of a volatile and possible vapour phase-active, phosphorus-based flame retardant component.

With regard to the first, we have demonstrated that the inclusion of small amounts of certain transition metal salts, notably those of zinc II and manganese II can reduce the onset of decomposition of ammonium polyphosphate from 304^{o}C to as low as 283^{o}C in the case of 2%(w/w) manganese II sulphate addition [6]. When applied in a back-coating formulation with APP, the presence of metal ions increases LOI values slightly from 25.1 for APP-only coated cotton to 26.6 in the presence of 2% manganese acetate, for example. However, all coated fabrics still failed the simulated small flame ignition version of BS 5852 [5], which is not perhaps surprising since our earlier research indicated that an LOI value for a coated cotton fabric above 26 and closer to 29 was required to sustain a pass. However, it was noted that the presence of the transition metal salt reduced the width of the charring area subjected to the flame source when compared with the APP-only sample. It should be pointed out, however, that even if passes had been obtained, the problem of durability to water soaking would still remain.

An extension of the first strategy above may be considerd to be the possible sensitisation using nanoparticulate additives. The inclusion of nano-particles in coating formulations has been investigated by Bourbigot et al [7, 8]. Both nanoclay and polyhedral oligomeric silsesquioxanes (POSS), when present alone in polyurethane coatings applied to polyester and cotton fabrics, were found to reduce peak heat release values of back-coated fabrics, although neither increase ignition times nor reduce extinction times. In fact the converse tended to be the case. Subsequent work by us [9] has shown that the introduction of nanoparticulate clays has no beneficial effect to a back-coating polymeric film and the introduction of fumed silica to a flame retarded back-coating formulation reduces its effectiveness.

In this paper, we focus upon strategy (iii) above and report the effects of introducing volatile phosphorus-containing agents to various back-coating formulations applied to coated fabrics. In addressing the need for such vapour phase activity, it must be remembered that the generally poor performance of all APP-containing coated fabrics is associated with the our earlier observation that enhanced char formation alone at the rear of a fabric is insufficient to prevent burning of the front face [6]. The obvious way of remedying this situation is to enable phosphorus-containing species to be rendered volatile and so enter the flame chemical reactions in a manner similar to bromine-containing retardants. However, if is this were to be effected, there is always the question of the flame retarding efficiency of such volatile species. The literature is not very helpful in this respect with usually only indirect evidence of vapour phase activity being cited. For instance Rohringer et al [10] have proposed that the relatively superior flame retarding efficiency of THPC-based flame retardants applied to polyester-cotton blends may be associated with the evolution of volatile phosphine oxides, which then act in the vapour phase and retard the burning polyester component unlike phosphonopropionamide-based treatments. Wiles et al [11] have also provided evidence that the flame retarding efficiency of now-banned tris (2,3-dibromopropyl) phosphate or “tris” ,when applied to polyester, is also a consequence of derived phosphorus species acting in the vapour phase. Hastie and Bonnel [12] used spectroscopic and high pressure sampling mass spectrometry to study possible flame inhibition effects of a number of phosphorus-containing compounds including trimethyl phosphate, phosphoryl choride and triphenylphosphine oxide. These were mixed with methane and propane fuels to observe their respective effects on flame behaviour. Flame inhibition was noted in diffusion flames burning in air, although in premixed flames (with air), some P-containing additives could increase flame strength. These same experiments indicated previous considerations that the $PO^{\cdot}$ radical was the predominant species in flames would have to be revisited since now it appeared that the $HPO_2^{\cdot}$ radical was more significant; the formation of this relatively stable radical is considered to be formed by the reaction:

$HPO^{\cdot} + H^{\cdot} + X = HPO_2^{\cdot}$

where X is a third body major flame component and that this then interacts with $H^{\cdot}$ and $OH^{\cdot}$ radicals as follows:

$HPO_2^{\cdot} + H^{\cdot} \rightarrow PO^{\cdot} + H_2O$

$HPO_2^{\cdot} + H^{\cdot} \rightarrow PO_2^{\cdot} + H_2$

$HPO_2^{\cdot} + OH^{\cdot} \rightarrow PO_2^{\cdot} + H_2O$

which interfere with the main flame propagation reactions. More recent work by Babushok et al [13] concerning the inhibition of alkane combustion in premixed flames suggests that in the vapour phase, phosphorus may be more effective than halogen. Based on these observations, it was decided to examine the effects of adding a number of selected and potentially volatile phosphorus-containing species into back-coating formulations.

EXPERIMENTAL

Materials

Flame retardants were all phosphorus-containing and were supplied largely as commercial or technical grade (Aldrich Chemicals) samples, see Table 1. These were ammonium polyphosphate as Antiblaze MCM (Albemarle, formerly Rhodia Specialities), melamine phosphate Antiblaze NH and phosphorylated pentaerythritol NH 1197 (Chemtura, formerly Great lakes Chemical Company), melamine and the potentially volatile retardants: monomeric cyclic phosphate Antiblaze CU (Rhodia Specialites), tributyl phosphate (TBP), triphenyl phosphonate (TPP) and triphenylphosphine oxide (TPPO), the oligomeric phosphate-phosphonate Fyrol 51 (Akzo). The formula for Fyrol 51 is $H\text{-}(O.CH_2.CH_2 .O.P(O)(OCH_3))_{2x}. (O. CH_2.CH_2 .P(O)(CH_3))_x .O.CH_2 .CH_2 .OH$ and is suggested by Akzo as a back-coating flame retardant although its market has been mainly as a reactive flame retardant for resin-treated paper air filters. Recently, Fyrol 51 has been renamed Fyroltex HP

and this has the subject of recent research with regard to its potential for flame retardant finishing of cotton and cotton/synthetic fibre blends by Yang et al [14, 15].

The resin used was a typical acrylic copolymeric formulation for back-coatings T122 (Noveon Inc.). Ancillary chemicals included the surfactant Performax 11297 (Noveon Inc.) for stabilising resin emulsions in the presence of phosphorus-containing flame retardants, the coating formulation thickener Carbopol JNC and foam stabiliser BEV681F (Noveon Inc).

100% commercially bleached cotton fabrics with an area densities 220 gm^{-2} and 360 gm^{-2} and a commercial plain woven 100% polypropylene fabric with area density of 260 gm^{-2} were used for coating experiments without further treatment

Back-coating formulation and application

Polymer emulsions of the acrylic copolymeric resin Noveon T122 surfactant (Performax 11297) were prepared and introduced on to cotton or polypropylene fabric samples as previously described [6] along with a proprietary de-foamer supplied by Noveon Inc. The generic back-coating formulation is shown in Table 2. Lighter weight cotton and polypropylene fabrics were coated using the k-bar technique with a No.4 k-bar giving approximately 30% dry formulation add-on by weight of fabric [5, 6]. The fabrics were dried at 100°C and cured at 150°C both for 3 minutes. The heavier weight cotton fabric (360 gm^{-2}) 30 cm wide samples were coated using a Web Processing (UK) laboratory bench-top coating unit with a constant doctor blade height of 300µm. These were dried at 110°C and cured at 150°C both for 3 minutes.

Flammability measurement

Limiting oxygen index measurements were undertaken as previously described [4-6]. A simulated version of the “match” ignition source in BS5852:1979:Part I described previously was used [4, 5] to test the ignition resistance and potential fire barrier properties of experimentally coated fabrics. In this simulated test, a piece of non-flame retardant polyurethane foam of 220 × 150 × 22 mm (density of 22kg/m^3) was used as the filling part of the composite to be tested. The coated fabric was cut into 220 × 150mm pieces and pinned on to the surface of the foam having dimensions above suitable for testing in a vertical orientation according to BS5438: 1989. The composite was mounted with the fabric on the face of the foam and the gas burner in BS5438: 1989, was used as a substitution for the butane tube burner in BS5852. With a flame height adjusted to 40mm as specified in BS 5438, this was applied parallel with the composite face for 20 seconds and then removed. If the composite continued to flame for more than 2 minutes or produced externally detectable amounts of smoke, heat or afterglow 15 minutes after removal of the ignition source, a “fail” was recorded for the test result, otherwise a “pass” result was reported.

Thermal analytical procedures

Simultaneous DTA/TGA experiments were undertaken using a TA Instruments SDT 2960. Samples (10mg±1mg) were analysed from ambient to 1000°C under flowing air (100ml/min) at a heating rate of 20°C/min.

RESULTS AND DISCUSSION

Phosphorus mobility in back-coated formulations

Four potentially volatile phosphorus flame retardants were selected based on their reported boiling or decomposition data and these were the monomeric cyclic phosphate Antiblaze CU (mass loss occurs above 197^{o}C [5]), tributyl phosphate (TBP) (m.pt.= -80^{o}C, b.pt. = 289^{o}C with decomposition), triphenyl phosphate (TPP) (m.pt. 48-52^{o}C, b.pt. 244^{o}C at 10mm Hg, 5% weight loss at 208^{o}C) and triphenylphosphine oxide (TPPO) (m.pt. 156-158^{o}C), this last being one studied by Hastie and Bonnel [12]. Their respective TGA responses are shown in Figure 1 from which it can be that the tributyl phosphate starts to lose mass (ie produces volatiles) at about 150°C. Since the leading sponsoring company was interested in back-coating both cotton and polypropylene fabrics, TBP was deemed to be most suitable since it would start to volatilise below the melting point of polypropylene (~165^{o}C) and well below the ignition temperature of cotton (~350^{o}C). A previously reported drawback of using liquid flame retardants such as Antiblaze CU is the tackiness caused to the final coating [4, 5]. However, the lower levels of tributyl phosphate to be used in the following experiments suggested that this factor would be less of a problem.

Three formulations were generated based on the generic formulation in Table 2, all containing 100 dry mass units of the acrylic copolymeric resin Noveon T122 and 12.3 dry units surfactant (Performax 11297) to stabilise the resin emulsion against the added flame retardant. Because of its particular efficiency as a char-former on back-coated polypropylene fabrics, the main char-forming flame retardant selected was the intumescent NH 1197 comprising phosphorylated pentaerythritol [5]. This was studied in the absence and presence of a volatile retardant and formulations were as follows while maintaining a constant total of 250 dry mass units:

- 250 dry mass units NH1197
- 200 dry units NH1197, 50 dry units tributyl phosphate
- 150 dry units NH1197, 100 dry units tributyl phosphate

Due to the liquid state of the tributyl phosphate, it was difficult to increase the dry unit content beyond 100 parts as this produced a very tacky coating as anticipated at these higher levels. The above formulations were repeated with triphenyl phosphate replacing the tributyl phosphate. While TPP is a solid thereby removing the tackiness problem, it should volatilise during ignition and possibly show vapour phase activity, although as shown above, it has a higher decomposition point (see Figure 1) and also has a tendency to agglomerate thus producing a very granular back-coating formulation, which prevents even coating. Formulations were back-coated using k-bars on to the 220 gm^{-2} cotton and 260 gm^{-2} polypropylene fabrics respectively. It must be noted that in deriving the optimum ratio for the formulations, the add-on was allowed to vary with respect to the substrate and coating formulation.

The back-coated samples were tested for LOI and selected ones were then tested using the small-scale simulation test of BS5852 after subjecting to a 40^{o}C water-soaking test for 30 minutes. Because of the difficulty of evenly coating larger fabric samples with formulations containing TPP, only LOI values were determined since testing to the simulated small flame test would not enable repeatable results to be obtained. Table 3 lists the results for both tests. From both LOI and simulated BS 5852 test results, it would seem that the partial replacement of the char-forming retardant NH 1197 by the volatile TBP and less volatile TPP gave back-coated cotton samples that showed improved performance with the dry mass ratio formulation of 200:50 giving the highest LOI values. It is interesting to note that while the previously noted agglomerating effect of TPP at 100 parts presence resulted in a high add-on of 104%, this almost doubled total flame retardant presence with respect to fabric has minimal effect on LOI. This suggests that once the flame retardant presence in the back-coating is sufficient to raise the fabric LOI to just above 26, this represents an asymptotic maximum value. A similar position may exist for the back-coated polypropylene samples except that this maximum value is just above an LOI value of 22.

However, while LOI values for all back-coated cotton samples are in excess of 26.0, the presence of a volatile agent such as TBP along with the char-promoting phosphorylated pentaerythritol derivative, NH 1197 is necessary to pass the simulated match test after a water soak. This result would suggest that the presence of a volatile phosphorus-containing component improves flame extinction during the front face ignition in the simulated BS 5852 test. This same effect is not seen in the polypropylene fabrics which have relatively low LOI values and excessive thermoplasticity with melting and this latter effect is not overcome or supported by the char-promoting elements within the back-coating. In fact the additions of TBP or TPP have little effect on the overall LOI with respect to back-coated PP fabrics containing only NH 1197; however, the 200:50 NH 1197:TPP only just failed the simulated BS 5852 test in spite of an LOI of only 21.5.

Phosphorus retention in fabric chars

In order to study whether phosphorus present in the flame retardant in a back-coating remained in the char or entered the vapour phase, a series of experiments was designed to enable phosphorus contents to be determined in charred samples of back-coated samples after exposure in air to a range of temperatures. The following four formulations were examined:

- ammonium polyphosphate (Antiblaze MCM)
- melamine phosphate (Antiblaze NH)
- cyclic phosphonate (Antiblaze CU)
- oligomeric phosphate-phosphonate (Fyrol 51)

each containing 250 parts by weight of flame retardant and 100 parts dry weight of polymer as shown in Table 1. For the two liquid retardants, Antiblaze CU and Fyrol 51, a second set of back-coatings each containing only 100 parts was prepared. All formulations required two surfactants present, one to stabilise the polymer dispersion (Performax 11257) and the other BEV681F (Noveon) to stabilise a foamed structure in order to apply them as evenly as

possible. In these experiments the heavier cotton fabric (360 gm^{-2}) was used to yield higher char masses and all coatings were applied as foams using a bench-top coating machine with respective dry add-ons listed in Table 4. In order to produce chars having different thermal histories, back-coated samples of known weight were then placed in a furnace at 300, 400, and 500 and 600^{o}C for 5 minutes in an air atmosphere. It must be emphasised that these experiments were not intended to simulate actual combustion conditions but were designed to create chars having residual phosphorus contents that would be dependent on the volatility of the phosphorus-containing moeities present. After exposure and cooling, charred samples were weighed and a phosphorus determination within of each charred sample was undertaken in the laboratories of Rhodia Consumer Specialities, Oldbury, UK according to their standardised procedure. Plots of phosphorus and residual sample masses are plotted in Figures 2-7 for each of the six formulations above. Included in each is the theoretical phosphorus present in each residue assuming that all phosphorus applied in the back-coating formulation is retained within each char. It is evident that in all samples, the original phosphorus levels with respect to the total mass of back-coated cotton will increase if the original phosphorus is retained in the charred residue of increasingly reduced weight as exposure temperature increases. These values are calculated from the known respective coating add-ons, retardant contents, phosphorus percentages within each retardant and the residual sample weights. In each set of plots for each formulation it may be seen that at each temperature, differences in phosphorus contents (ΔP) exist between observed and theoretical and these are quantified in Table 4. Assuming that negative ΔP values represent experimental error associated with an approximately zero value, then these results suggest that those flame retardants that may be exerting predominantly condensed phase activity, such as APP and melamine phosphate, do in fact show minimal ΔP values since all phosphorus essentially remains in respective residues. However, both liquid flame retardants have ΔP values that increase with respective contents in each formulation as well as temperature of exposure. Thus loss of phosphorus is occurring during charring by

volatilisation. Whether or not this volatile phosphorus has a chemically-active, vapour phase retardation effect cannot be established from these results, however.

TGA and LOI analysis have been carried out on all six coated samples and Table 5 shows respective LOI values and char residues at 500°C. The previous ΔP values expressed as a percentage of respective sample theoretical P levels present in chars at 500°C are included as ΔP' values for comparison. As a general rule it may be suggested that high LOI and residue values coupled with low ΔP' values indicate condensed phase activity, whereas high LOI and ΔP' but low residue values suggest predominant vapour phase activity. Not only do the two volatile flame retardants show the highest LOI values with respect to APP and melamine phosphate-containing formulations, but they also show the lowest TGA-derived char and highest ΔP values thereby suggesting considerable vapour phase activity. Conversely, the Antiblaze NH and MCM-containing samples show high LOI values along with highest char and lowest ΔP levels, thereby suggesting condensed phase activity. The Fyrol 51-containing sample result is interesting in that a high LOI is obtained with a char residue in between that of CU and MCM. This suggests it may have a two-phase activity rather than being predominantly active in one or the other.

Addition of volatile components to APP

Based on our original successes with APP [4, 5] and aware that using variants of increased insolubility may compromise its effectiveness in back-coatings, a final set of experiments was undertaken based on the outcomes of the above including the addition of melamine (Mel), known to volatilise by sublimation at temperatures above 400^{o}C. Formulations as listed in Table 6 were prepared comprising 250 parts total flame retardant as in Table 2 but divided equally in mass proportions determined by the number of components present , coated on to cotton and then tested for LOI and to the simulated BS 5852: Part 1: Source 1 test before a water-soak. In the latter, three flame application times were used to demonstrate the superior

behaviour of these compositions. The inclusion of melamine appears to be responsible for the raising of LOI values of all samples to exceed 27. It is notable that the APP/melamine formulation fails at flame application times above 20s but those containing volatile phosphorus-containing agents continue to pass.

Unfortunately, similar high performance was not observed after coated fabrics had been subjected to a water-soak at 40^{o}C as shown in Table 7. The retentions of active flame retardants after water soaking were obtained by weighing before and after and are presented as weight percentages. Although retention of the applied formulations often exceeded 70%, it is clear that the major part of the losses will be the APP component. However, this could be reduced by use of higher degree of polymerisation APP types, those having microencapsulation coatings and use of resins having higher levels of hydrophobicity. Clearly, these are areas worthy of further research.

CONCLUSIONS

It is clear from the above set of experiments that if effective phosphorus-containing replacements are to be found for decaBDE and similar bromine-containing flame retardants in back-coatings, then not only has the water durability issue to be solved, but more importantly, it must be realised that simple condensed phase retardant systems are ineffective by themselves. Furthermore, such systems rely on char-generation of both the bonding resin and the fibres present in the fabrics with char-forming reactions of the latter being specific to each fibre type present. Vapour-phase systems such as the established bromine-containing formulations are not fibre and textile substrate specific because of the efficiency with which released bromine radicals terminate the flame chemistry chain reactions common to all burning organic polymers. Thus, if a phosphorus-containing flame retardant or a component thereof can be volatilised either as a decomposition product or by evaporation during the impingement of an igniting flame to the front surface of a back-coated fabric, then

there is evidence of improved performance. The system based on an intumescent phosphorylated pentaerythritol derivative in combination with relatively volatile tributyl phosphate enables a back-coated cotton fabric to pass the small flame ignition source simulation of BS 5852 Part 1:1979 even after a 40^{o}C water soak as required by UK regulation [1]. In this formulation, therefore, both the need for vapour phase activity and water soak durability have been achieved. The addition of the nitrogen-containing melamine adds further to the overall volatilising behaviour of the overall back-coating formation and this also adds to the observed flame retardancy as well as being water insoluble.

In conclusion, therefore, the above experimental results suggest that further investigation of potentially volatile phosphorus-containing and nitrogen-containing retardants and their possible vapour phase activity is essential if the replacement of bromine-containing flame retardants is to be realised technically within the near future.

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REFERENCES

1. Anon. (1988), Consumer Protection Act (1987), the Furniture and Furnishings (Fire) (Safety) Regulations*, 1988*, SI1324 (1988), HMSO, London.
2. National Academy of Sciences. (2000). Toxicological risks of selected flame-retardant chemicals. Sub-committee on Flame-retardant Chemicals of the United States National Research Council, Washington, DC; National Academy Press, Washington, DC, USA.
3. Anon. (2003). European Union Risk Assessment Report for bis(pentabromodiphenyl) ether, European Chemicals Bureau, (closed 26th May 2004) : www.bsef.com
4. Wang M., Horrocks A. R., Horrocks S., Hall M. E. and Pearson J. S. (2000). *J. Fire Sci.*, **18**: 265-294.
5. Horrocks A. R., Wang M. Y., Hall M. E., Sunmonu F. and Pearson J S. (2000). *Polymer Int.* **49**:1079-1091.

6. Davies P. J., Horrocks A. R. and Alderson A. (2005). *Polym Degrad. Stab.,* **88** (1): 114-122
7. Bourbigot S., Devaux E., Rochery M. and Flambard X. (2002). In proceedings 47th International SAMPE Symposium, May 12-16, 2002: 1108-1118
8. Devaux E., Rochery M. and Bourbigot S. (2002). *Fire Mater.,* **26** (4-5): 149-154
9. Horrocks A. R., Davies P. J., Kandola B. K. and Alderson A. (2007). In proceedings of Flame Retardant Polymers and Materials, FRPM05, Berlin, September 2005, in press
10. Rohringer P., Stensby T. and Adler A. (1975). *Text. Research J.,* **45**: 586
11. Day M., Ho K., Suprunchuk T. and Wiles D. M. (1982). *Canadian Textile J.,* **99** (5): 39
12. Hastie J. W. and Bonnell D. W. (1980). Molecular chemistry of inhibited combustion systems', Report NBSIR 80-2169, National Bureau of Standards, Gaithersburg, MD., USA.
13. Babushok, V.; Tsang, W., (2000). *Combust. Flame*, **124**: 488-506.
14. Wu W.D, Yang C.Q. (2007). *Polym. Degrad Stab.,* **92**(3): 363-369.
15. Yang H. and Yang C.Q. (2005). *Polym Degrad Stab*., **88**(3): 363-370.

Tables:

Table 1: Flame retardants used and their chemical characteristics

Chemical name	Manufacturer/supplier	Commercial name
Ammonium polyphosphate	Albemarle, formerly Rhodia Specialiaties	Antiblaze MCM
Melamine phosphate	Albemarle, formerly Rhodia Specialiaties	Antiblaze NH
Monomeric cyclic phosphonate	Rhodia Specialities	Antiblaze CU
Phosphorylated pentaerythritol	Chemtura, formely Great Lakes Chemical Company	NH1197
Oligomeric phosphate-phosphonate	Akzo	Fyrol 51
Melamine	Aldrich Chemicals	
Tributyl phosphate (TBP)	Aldrich Chemicals	
Triphenyl phosphonate (TPP)	Aldrich Chemicals	
Triphenylphosphine oxide (TPPO)	Aldrich Chemicals	

Table 2: Generic back-coating formulation

Component	Dry Units	Wet Units
Resin	100	204
Defoamer	2	4.7
Flame retardant	250	250
H_2O	0	131
TOTAL	352	589.7

Table 3: Flammability testing results of back-coated cotton and polypropylene fabrics after a 40°C water soak treatment

Formulation	Fabric	Dry add-on, %	Simulated BS 5852	LOI	Comment
NH-1197 (250)	Cotton	41	-	26.1	
NH-1197 (250)	PP	64	-	22.4	
NH-1197 (200) TBP (50)	Cotton	37	Pass	26.7	
NH-1197 (200) TBP (50)	PP	57	Fail	21.5	Visual observation suggests near to pass
NH-1197 (150) TBP (100)	Cotton	52	Pass	26.3	Char length greater than 200:50 analogue
NH-1197 (150) TBP (100)	PP	66	Fail	22.4	
NH-1197 (200) TPP (50)	Cotton	49	-	26.7	
NH-1197 (200) TPP (50)	PP	53	-	21.5	
NH-1197 (150) TPP (100)	Cotton	104	-	26.4	High add-on is a consequence of agglomeration of solids
NH-1197 (150) TPP (100)	PP	47	-	21.3	

Table 4: Difference between actual and theoretical phosphorus contents (ΔP) of charred back-coated cotton fabrics

Flame retardant/parts by weight	Initial add-on, %	ΔP, % 300°C	400°C	500°C	600°C
Antiblaze MCM/250	13.9	0.41	1.35	4.93	3.07
Antiblaze NH/250	11.0	-0.16	-0.24	0.9	1.87
Antiblaze CU/250	11.9	1.91	4.77	10.51	23.95
Antiblaze CU/100	22.3	0.57	1.87	5.36	12.28
Fyrol 51/250	16.6	1.62	2.78	7.64	7.59
Fyrol 51/100	16.1	0.44	1.52	3.05	7.46

Table 5: TGA and LOI results for back-coated 360 gm^{-2} cotton fabrics

Flame retardant/parts by weight	LOI	TGA Residue (%) at 500°C	ΔP' (%) at 500°C
Antiblaze MCM/250	23.2	30.9	39.3
Antiblaze NH/250	20.8	26.1	24.3
Antiblaze CU/250	26.3	18.3	70.1
Antiblaze CU/100	23.6	18.8	64.1
Fyrol 51/250	26.1	-	70.8
Fyrol 51/100	24.9	25.0	46.3

Table 6. Flammability testing for mixed flame retardant formulations (pre-water soak)

	Add-on (%)	LOI	Indicative BS5852 "match" Source 1 test		
			10s	20s	30s
APP / Mel	52	27.1	Pass	Pass	Fail
APP / Mel / CU	37	27.9	Pass	Pass	Pass
APP / Mel / F51	52	29.6	Pass	Pass	Pass
APP / Mel / TBP	43	28.6	Pass	Pass	Pass

Table 7. Durability Results and Flammability Testing (post water soak)

	Formulation retention		Indicative BS 5852 Source 1 test	
	Add-on (%w/w)	**Add-on retention (%)**	**Flame application time, s**	
			10	20
APP/Mel	39	75	×	-
APP/Mel/CU	19	52	×	-
APP/Mel/F51	34	65	✓	×
APP/Mel/TBP	34	78	×	-

Note: "✓" denotes a pass, "×" denotes a fail and "–" denotes no test undertaken

Figure Legends:

Figure 1: TGA responses of Antiblaze CU, tributyl phosphate (TBP), triphenyl phosphate (TPP) and triphenylphosphene oxide (TPPO) under nitrogen

Figure 2: Phosphorus concentrations and residual weights for back-coated cotton samples containing 250 dry parts Antiblaze MCM in the formulation

Figure 3: Phosphorus concentrations and residual weights for back-coated cotton samples containing 250 dry parts Antiblaze NH in the formulation

Figure 4: Phosphorus concentrations and residual weights for back-coated cotton samples containing 250 dry parts Antiblaze CU in the formulation

Figure 5: Phosphorus concentrations and residual weights for back-coated cotton samples containing 100 dry parts Antiblaze CU in the formulation

Figure 6: Phosphorus concentrations and residual weights for back-coated cotton samples containing 250 dry parts Fyrol 51 in the formulation

Figure 7: Phosphorus concentrations and residual weights for back-coated cotton samples containing 100 dry parts Fyrol 51 in the formulation

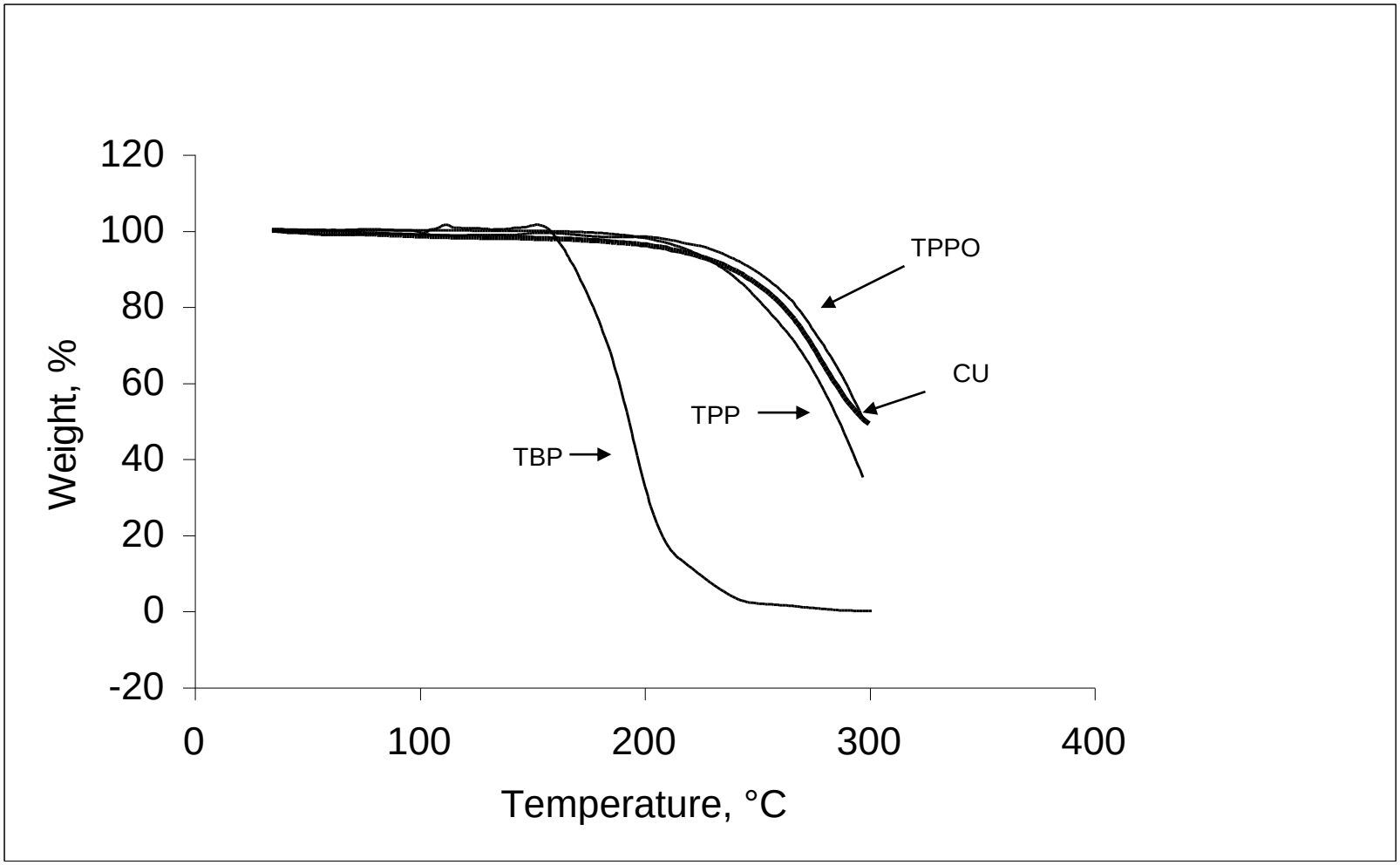

Figure 1: TGA responses of Antiblaze CU, tributyl phosphate (TBP), triphenyl phosphate (TPP) and triphenylphosphene oxide (TPPO) under nitrogen

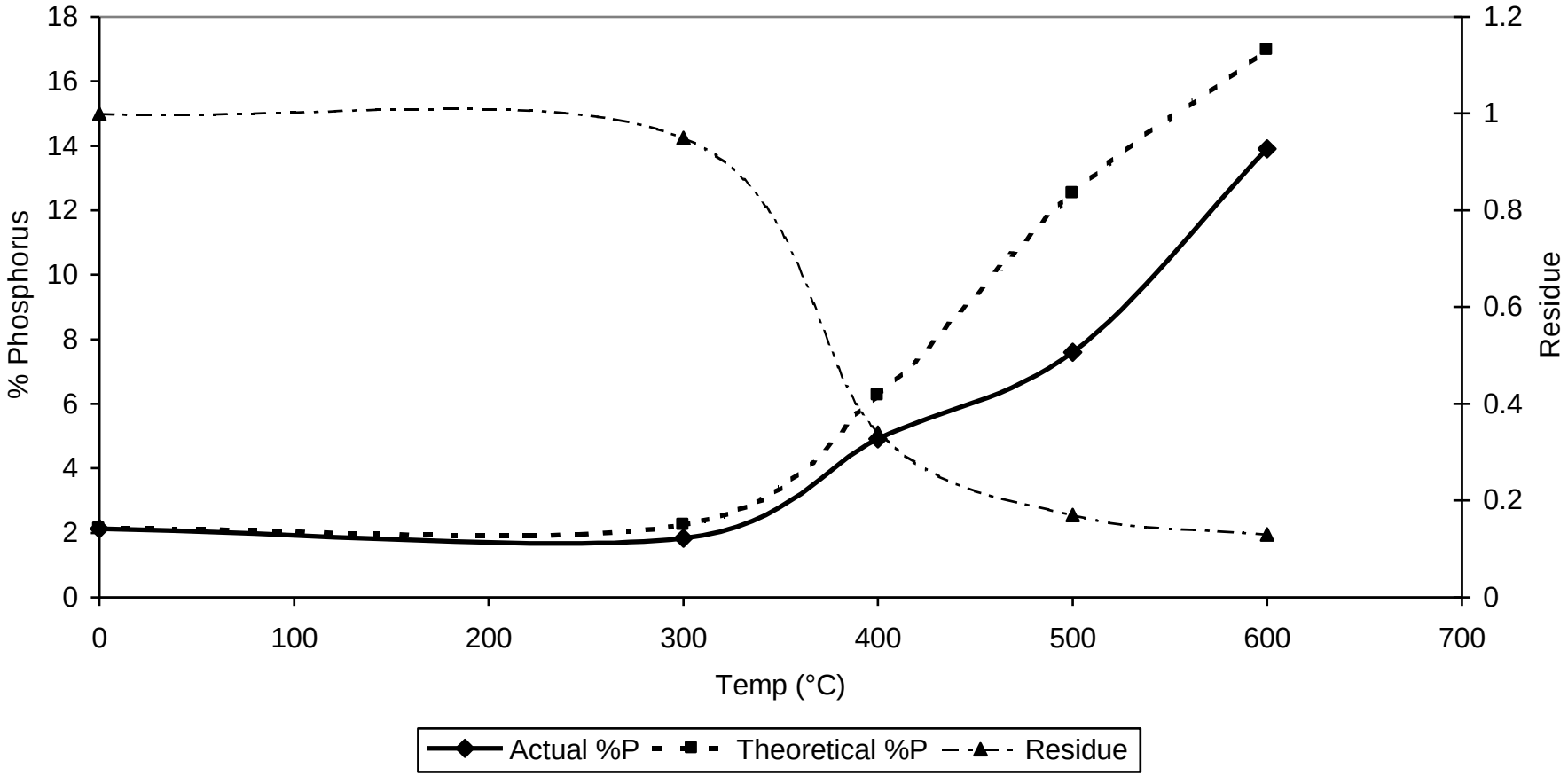

Figure 2: Phosphorus concentrations and residual weights for back-coated cotton samples containing 250 dry parts Antiblaze MCM in the formulation

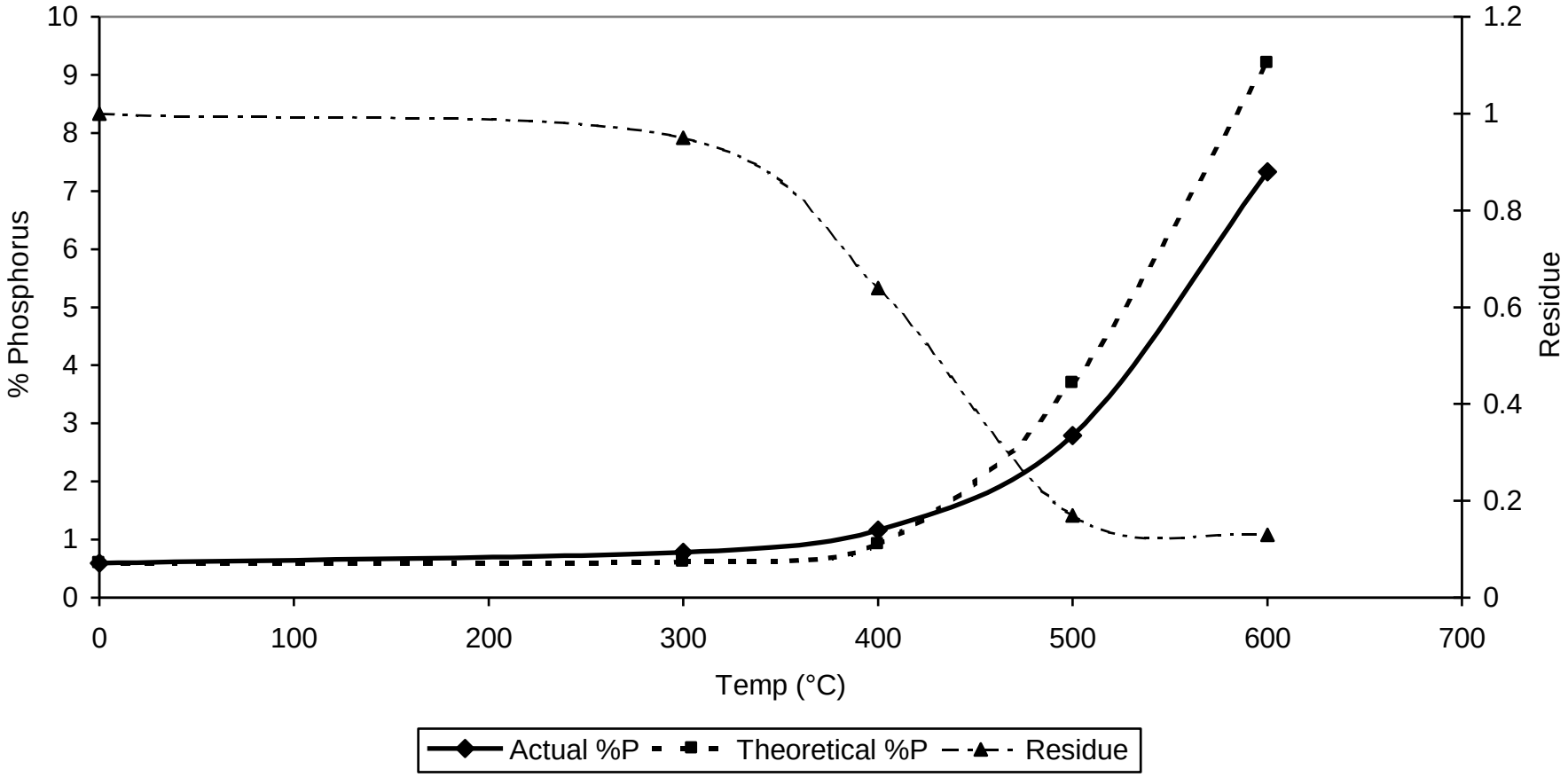

Figure 3: Phosphorus concentrations and residual weights for back-coated cotton samples containing 250 dry parts Antiblaze NH in the formulation

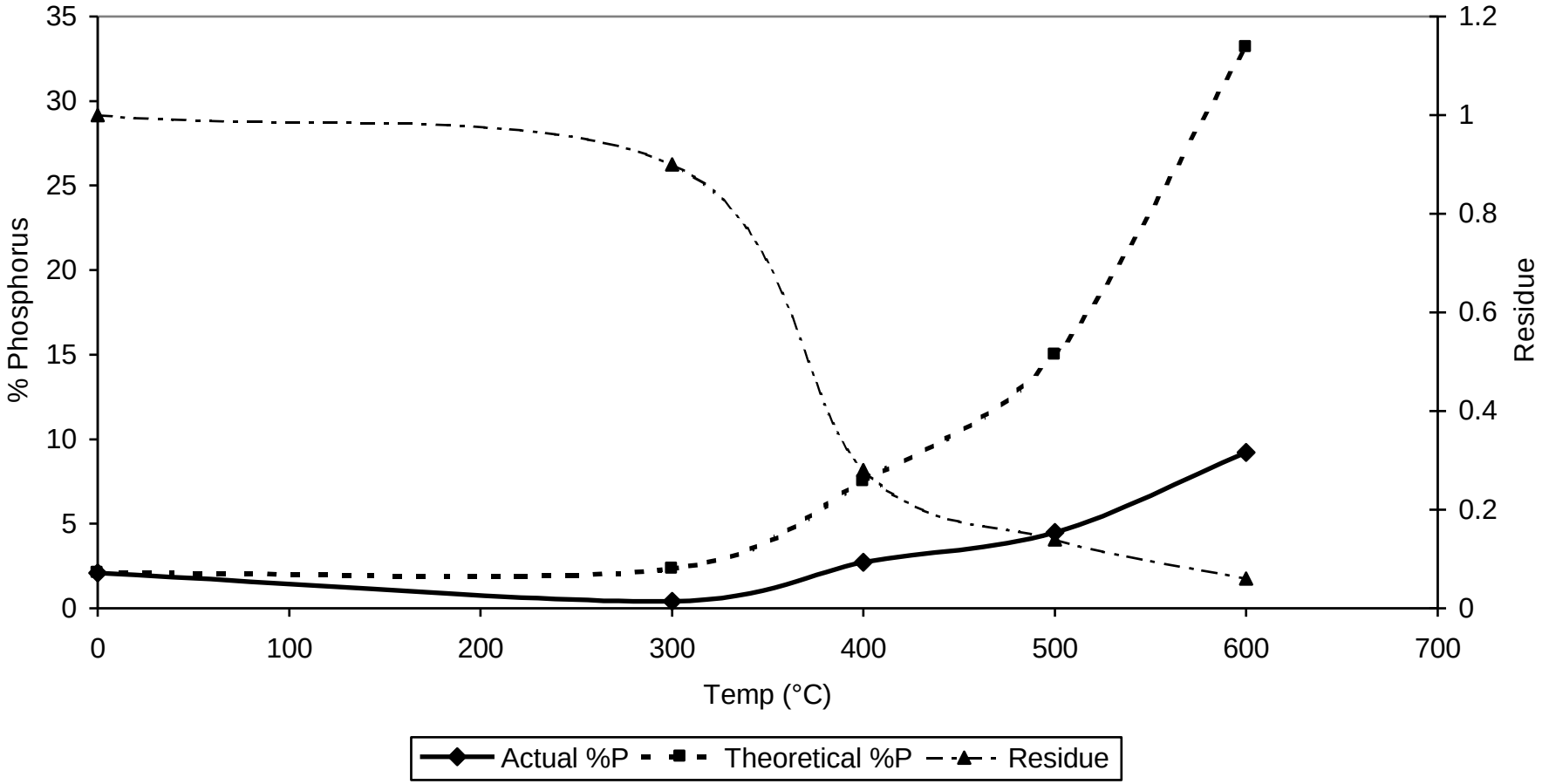

Figure 4: Phosphorus concentrations and residual weights for back-coated cotton samples containing 250 dry parts Antiblaze CU in the formulation

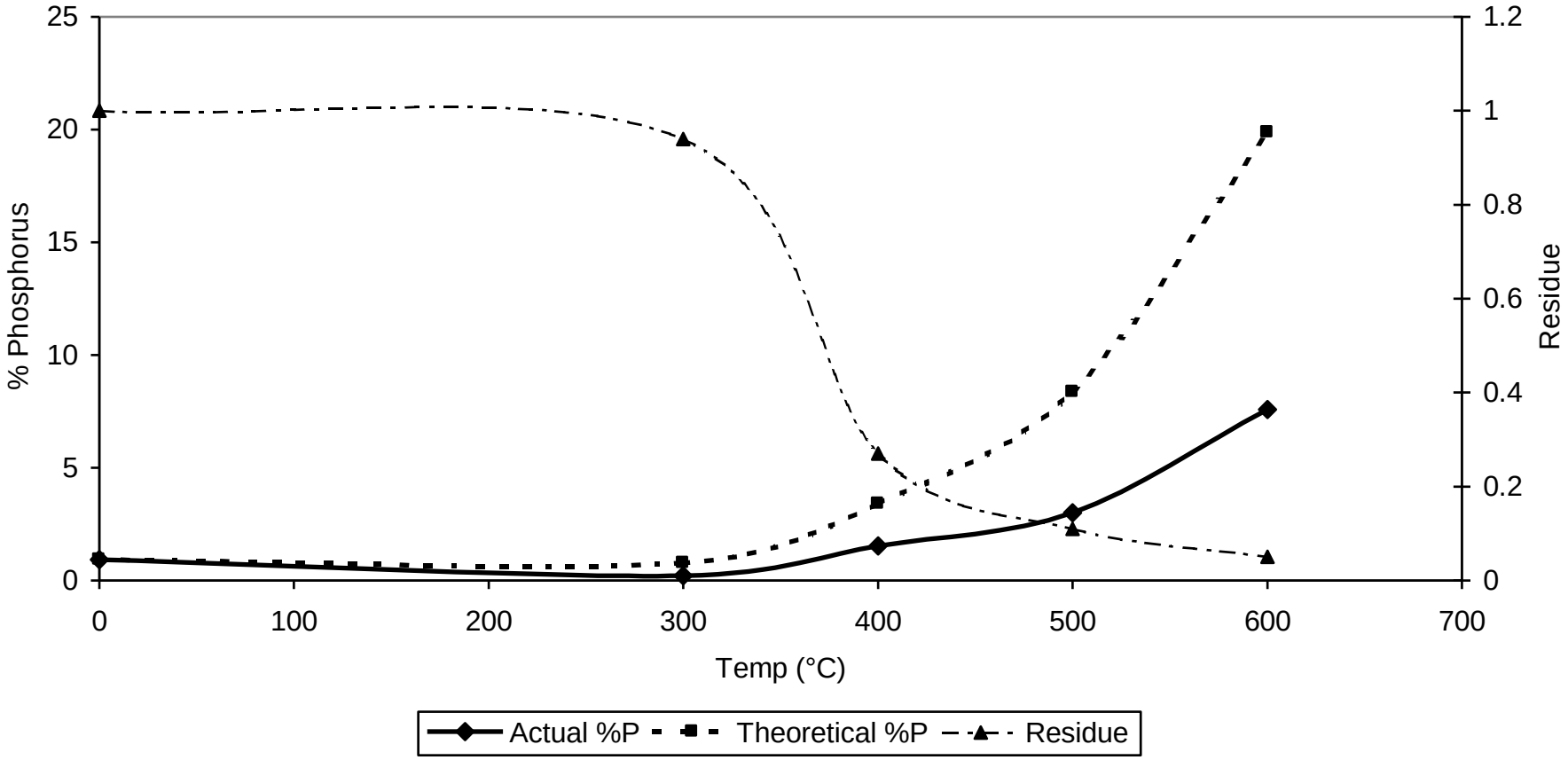

Figure 5: Phosphorus concentrations and residual weights for back-coated cotton samples containing 100 dry parts Antiblaze CU in the formulation

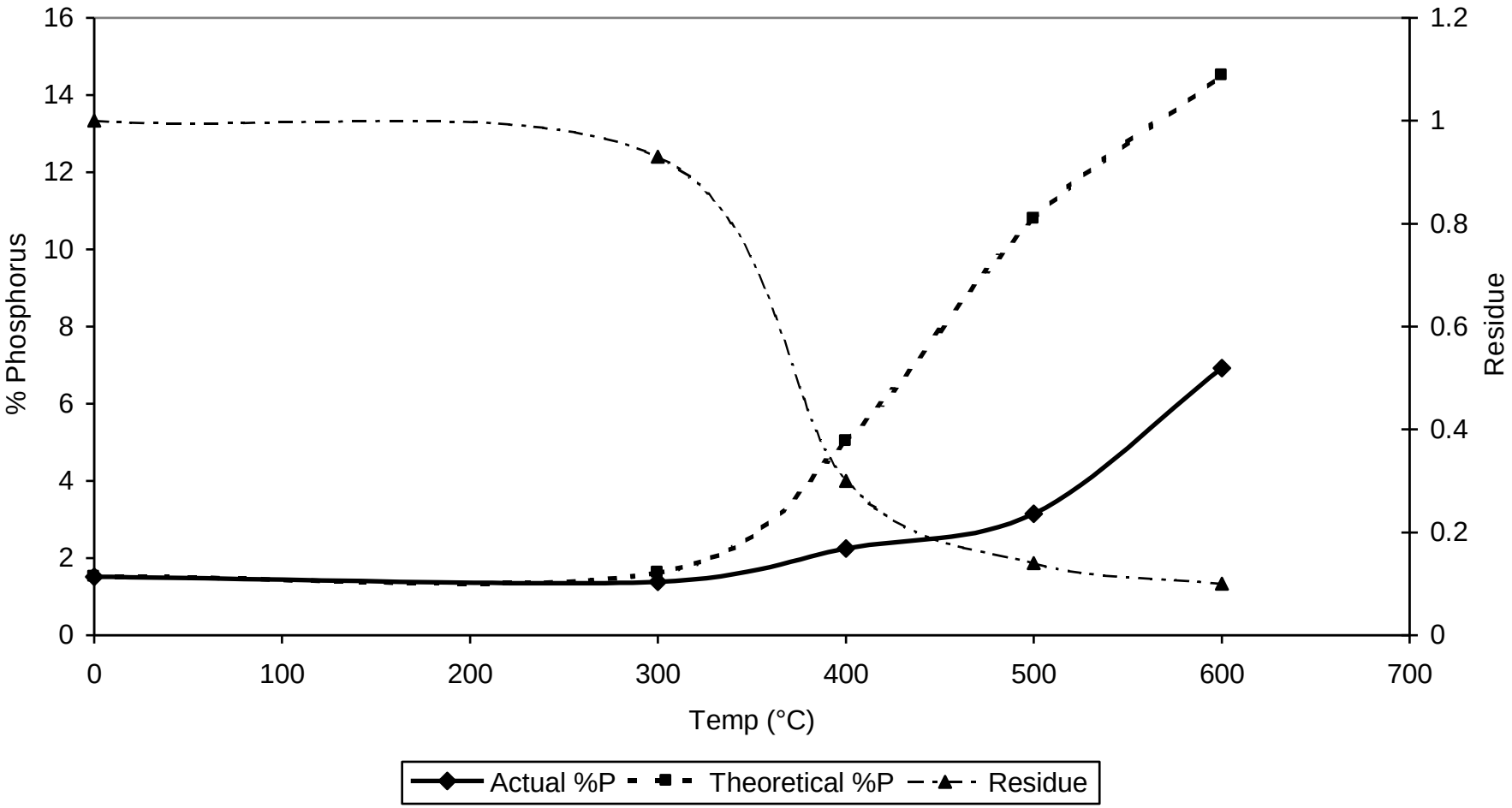

Figure 6: Phosphorus concentrations and residual weights for back-coated cotton samples containing 250 dry parts Fyrol 51 in the formulation

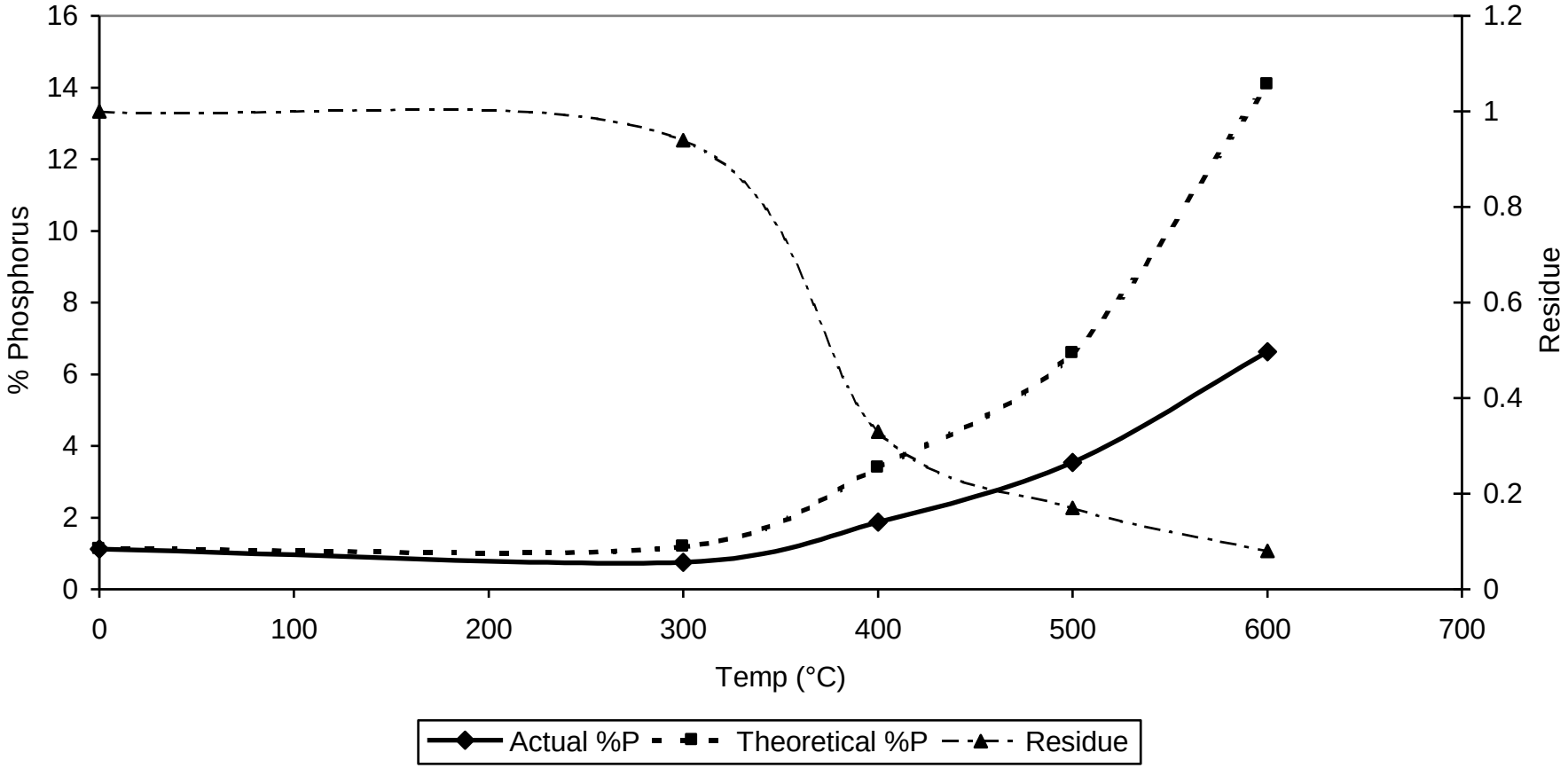

Figure 7: Phosphorus concentrations and residual weights for back-coated cotton samples containing 100 dry parts Fyrol 51 in the formulation